The Open University of Sri Lanka

Faculty of Natural Sciences

B.Sc./ B. Ed. Degree Programme

Department	: Chemistry
Level	: 4
Name of the Examination	: Final Examination
Course Code and Title	: **CYU5300 – Organometallic Chemistry**
Academic Year	: 2024/2025
Date	: 03 – 12 - 2024
Time	: 1.30 p.m. – 03.30 p.m.
Duration	: 02 hours
Index number	:

General Instructions

1. Read all instructions carefully before answering the questions.
2. This question paper consists of **04** pages containing **04** questions.
3. Answer **all four** questions. All questions carry equal marks.
4. Answer for each question should commence from a new page.
5. Draw fully labelled diagrams where necessary.
5. Relevant log tables are provided where necessary.
6. Having any unauthorized documents/ mobile phones in your possession is a punishable offense.
7. Use blue or black ink to answer the questions.
8. Circle the number of the questions you answered in the front cover of your answer script.
9. Clearly state your index number in your answer script.

01. (a) Give the IUPAC name of **$[(\eta^5\text{-}C_5H_5)Fe(\eta^1\text{-}C_5H_5)(CO)_2]$** **(10 marks)**

(b) Draw the structures of the following complexes. **(20 marks)**

(i) Tricarbonyl(η^4-cyclobutadiene)ruthenium

(ii) $[(\eta^4\text{-}C_7H_8)Fe(CO)_3]$

(c) (i) Determine the Valence Electron Count (VEC) of the following complex using the **covalent model.**

$$[(\eta^5\text{-}C_5H_5)W(\eta^3\text{-}C_5H_5)(CO)_2]$$

(Hint: Indicate in your workout, the electron contribution from each ligand, W is a group 6 element)

(ii) What is the coordination number of **W** in this complex?

(15 marks)

(d) Draw and identify the structure of each of the following compounds.

(i) $[Mn(CO)_6]^+$

(ii) $[PtCl_2(\text{cycloocta-1,5-diene})]$

(20 marks)

(e) Draw **all** possible isomers of the following complex **$[Co(H_2O)_2(ox)BrCl]^-$**, where ox is $^-O_2CCO_2^-$, which stands for oxalate. **(20 marks)**

(f) Describe the bonding between a metal and an alkynyl group (e.g. $-C{\equiv}CR$), use appropriate orbital diagrams. **(15 marks)**

02. (a) Arrange **PMe_3**, **PF_3**, and **PPh_3** in the order of increasing π-acceptability **(10 marks)**

(b) Draw the structure of **$[Ni(\text{cycloocta-1,5-diene})_2]$** and briefly explain the geometry and bonding of the complex (orbital diagrams are not required). **(20 marks)**

(c) How would you account for the variation in the C=C stretching frequencies in the following compounds? **(25 marks)**

Compound	ν(C=C) in cm^{-1}
Free $CH_2=CH_2$	1623
$[Ag(\eta^2\text{-}CH_2=CH_2)_2]BF_4$	1584
$[CpRh(\eta^2\text{-}CH_2=CH_2)_2]$	1493

(d) Explain the bonding between a metal and a **PR_3** ligand using orbital diagrams. **(20 marks)**

(e) Consider the following dissociative equilibrium. **(10 marks)**

$$[NiL_4] \rightleftharpoons [NiL_3] + L$$

Explain why the rate of dissociation is faster when L is PPh_3 than $PMePh_2$.

(f) State whether the following statements are true or false (T/F). **(15 marks)**

(i) $[Pt(PPh_3)_3]$ oxidatively adds PhI to give a square-planar complex $[PtPh(I)(PPh_3)_2]$

(ii) Oxidative addition of MeI is more facile to $[RhMe(CO)_2(PMe_3)]$ than $[RhMe(CO)(PMe_3)_2]$

(iii) trans-$[IrCl(CO)(PMe_3)_2]$ oxidatively adds p-$MeC_6H_4SO_2Cl$ to give the octahedral complex $[IrCl_2(O_2SC_6H_4Me\text{-}p)(CO)(PMe_3)_2]$

03. (a) (i) What is an agostic interaction?

(ii) Draw the structure of the complex **$[(\eta^5\text{-}Cp)Co(Et)(PMe3)]^+$** with an agostic-ethyl group. Draw the structure of the expected cobalt hydride that would be formed due to the cleavage of this agostic C–H bond **(20 marks)**

(b) The catalyst **$[IrCl(PMe_3)_3]$** reacts with H_2 to give the octahedral Ir(III) dihydride (**A**). Replacement of PMe_3 by **$MeCH=CH_2$** of (A) gives the olefincomplex (**B**). In the presence of PMe3, (**B**) undergoes migratory insertion to give the octahedral Markovnikov product (**C**). (**C**) reductively eliminates the alkane (**D**) to regenerate the catalyst **$[IrCl(PMe_3)_3]$.**

Write the molecular formulae of (**A**), (**B**), (**C**) and (**D**). **(40 marks)**

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(c) What is the major product formed by the cross-coupling reaction of PhBr with CH_2=CHSnBu_3 in the presence of the catalyst **[$Pd(PPh_3)_4$]**. **(10 marks)**

(d) (i) Define the terms Turnover number (TON) and Turnover frequency (TOF) **(10 marks)**

(ii) Treatment of PhI (2.0 mmol) with styrene (2.0 mmol) in the presence of the catalyst [$Pd(OAc)_2$] (0.0002 mmol) for 10 minutes gives the product stilbene (PhCH=CHPh) (1.80 mmol, 90% yield). What is the TON and TOF of this reaction? **(20 marks)**

04.

(a) $IrCl(N_2)(PPh_3)_2] + NMe_3$ ⟶ (Ligand substitution) **(10 marks)**

(b) all *trans* -$[PdI_2(Ph)_2(PPh_3)_2]$ $\xrightarrow{MeOH}$ (Reductive elimination) **(10 marks)**

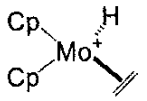
(c) *cis*-$[PtCl(Et)(PMe_3)_2$ $\xrightarrow{\Delta}$ (β–H abstraction) **(10 marks)**

(d) $[Fe(PMe_3)_4$ + 2 MeC≡CMe ⟶ (Oxidative coupling) **(12 marks)**

(e) $[IrCl(PPh_3)_3]$ $\xrightarrow{\Delta}$ (Cyclometallation) **(12 marks)**

(f) $[Cr(CO)_6]$ + Me^- ⟶ (Nucleophillic attack) **(10 marks)**

(g) $[(\eta^5\text{-Cp})(CO)_2Fe(\eta^1\text{-}C_5H_5)]$ + H^+ ⟶ (Electrophillic attack) **(12 marks)**

(h)  + PMe_3 $\xrightarrow[\text{2. Coordination}]{\text{1. 1,2-insertion}}$ **(12 marks)**

(i) $[(\eta^5\text{-}C_5H_5)_2WMe(\eta^2\text{–HC≡CH})]^+$ $\xrightarrow{Me^-}$ (Nucleophillic attack) **(12 marks)**